GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

Date: 20 March 1968

RESEARCH PROJECT INITIATION

Project Title: Chemistry of Carbanions

Project No.: B-1530

Project Director: Dr. Erling Grovenstein, Jr.

Sponsor: National Science Foundation

Agreement Period: From 1 April 1968 until 31 March 1970

Type Agreement: Grant GP-8309

Amount: $37,600 NSF Funds (B-1530)
12,133 GIT Contribution (E-1519)
$49,733 Total Budget

Grant Administrator

Dr. Donald A. Speer
Program Director
Chemical Dynamics Program
National Science Foundation
Washington, D. C. 20550

Reports Required

Annual - Short informal report
1 April 1969

Final - upon completion of project.

Note: Continuation of B-1559

Assigned to: School of Chemistry

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

April 1, 1969

Dr. Donald A. Speer
Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

Dear Dr. Speer:

Subject: Annual Report for NSF Grant GP-8309 upon "Chemistry of Carbanions" for period April 1, 1968 - March 31, 1969.

Neophyllithium [$PhC(CH_3)_2CH_2Li$] has been prepared in yields of some 80% by reaction of neophyl chloride with lithium metal in tetrahydrofuran solution at -65°. Careful examination of the products of carbonation of this organolithium preparation shows that it is only some 93.6% pure neophyllithium(I) contaminated with 6.4% of $PhCH_2C(CH_3)_2Li$(II). Upon long standing at -70° the quantity of II in this preparation slowly decreases. Upon warming such a preparation to -10° for one hour, all of II disappears and the quantity of I drops to 40%; in the neutral products from carbonation 19.3% of t-butylbenzene and 8.8% of isobutylbenzene appears. Our conclusion is that some 8% rearrangement (1,2-migration of phenyl) occurs during reaction of neophyl chloride with lithium metal. We believe that the migration occurs in an intermediate neophyl free radical since neophyllithium once formed is resistant to further 1,2-shift of a phenyl group. The present work indicates that the reaction of alkyl chlorides in ethereal solvents with lithium metal takes place at least in part by way of free radicals; this phenomenon has long been expected but strong evidence such as the present has been lacking.

Much work has been devoted to a study of the synthesis of alkylcesium compounds in ethereal solvents at low temperatures. Even at -60 to -110° n-butylcesium is highly unstable in tetrahydrofuran and dimethyl ether but slightly

GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT TERMINATION

Date: October 1, 1970

Project Title: Chemistry of Carbanions

Project No: B-1530

Principal Investigator: Dr. Erling Grovenstein, Jr.

Sponsor: National Science Foundation

Effective Termination Date: October 1, 1970

Clearance of Accounting Charges: All acceptable charges have cleared.

All grant requirements have been fulfilled.

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more stable in diethyl ether. A 19% yield of n-butylcesium (likely admixed with n-butylpotassium) has been obtained after 15 min reaction of n-butyl chloride with the eutectic alloy of Cs-K-Na at -70°; under similar conditions but with $(n\text{-Bu})_2Hg$ in place of n-BuCl a 37% yield of n-butylcesium resulted.

The above experiments were performed by Mr. Y. M. Cheng. In January, Dr. Craig Smith began work under the present grant on the cyclopropylcarbinyl anion. We wish to learn how readily formed this anion is compared to allylcarbinyl anion and to learn how extensively deuterium label rearranges in  $CD_2:^-$.

Finally we are indebted to the National Science Foundation for permission to support Mr. Tomoo Shibata under the present grant for work in the area of organic photochemistry. This support has permitted us to complete some work which has long been in progress in our laboratory. A copy of our manuscript on "Photochemical Reactions of Dimethyl Acetylenedicarboxylate with Benzene and Naphthalene" is enclosed; this paper has been accepted for publication in the Journal of Organic Chemistry and is scheduled for publication in June.

The support of the National Science Foundation during the past year is greatly appreciated.

Sincerely yours

Erling Grovenstein, Jr.
Brown Professor of Chemistry

EG:eb
Enclosure

B-1530

Resumé of Progress to Date upon "Chemistry of Carbanions"

For Period April 1, 1968-September 30, 1969

NSF Grant GP-8309

by Erling Grovenstein, Jr., Principal Investigator

I. Preparation of Organoalkali Compounds with Use of the Alloys of Cesium and Potassium

Much effort has been spent toward improvement of methods of preparation of organoalkali compounds. In view of the thermal instability of many organopotassium compounds even in hydrocarbon media,[1] efforts have been directed toward preparation of organoalkali compounds at low temperatures. Toward this end the binary alloy[2] of cesium and potassium (Cs, 51 at. %; K, 49 at. %; mp -45°) has been utilized as well as the ternary alloy (Cs, 40.8 at. %, K, 47.4 at. %, Na, 11.8 at. %; mp -79°). The fluid nature of these alloys permits ready contact of a fresh surface of the metal with organic substrate; moreover at the low temperatures used the alloy is soluble in tetrahydrofuran as visibly demonstrated by the appearance of a pale blue color in the solvent. These alloys doubtlessly produce a mixture of organoalkali compounds of cesium and potassium (and sometimes sodium) whose composition is dependent upon the ratio of alloy to substrate. For brevity we will refer to the products produced as "organocesium" compounds.

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(1) R. A. Finnegan, Tetrahedron Letters, 429 and 851 (1963).

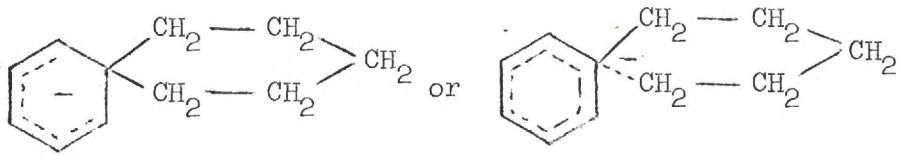
(2) C. Goria, Gazz. chim. ital., 65, 1226 (1935).

(3) F. Tepper, J. King, and J. Greer, "The Alkali Metals, An International Symposium Held at Nottingham on 19-22nd July, 1966," The Chemical Society, London, 1967, p. 23.

(a) Reaction with n-Butyl Chloride and Dibutylmercury. — Dropwise addition of n-butyl chloride over a three minute period to some 50% excess Cs-K-Na alloy with stirring for three more minutes in tetrahydrofuran at -70° gave, after carbonation, complete reaction of the n-butyl chloride but only 5.4% of valeric acid. If the reaction was stirred for nine more minutes before carbonation, the yield of valeric acid dropped to 2.4%. Butylcesium is, therefore, unstable in tetrahydrofuran even at -70°. In similar reactions in dimethyl ether and in diethyl ether, yields of valeric acid as high as 13 and 19% respectively have been obtained. Similar cleavage of dibutylmercury by Cs-K-Na, according to results from carbonation, gave 34% of butylcesium in tetrahydrofuran (13.5 minutes) and 37% in diethyl ether (15 minutes). Attempts to determine the nmr spectrum of butylcesium in diethyl ether were unsuccessful, apparently because of insolubility of this organoalkali reagent.

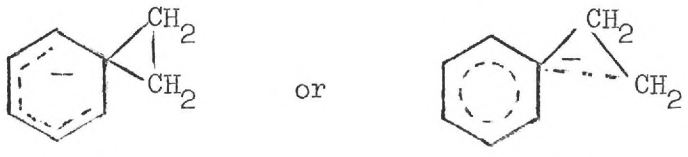
(b) Reaction with Neophyl Chloride. — Reaction of neophyl chloride with some 100% excess Cs-K-Na alloy at -66° in tetrahydrofuran for 13 minutes gave, upon carbonation, only 1.2% yield of $PhC(CH_3)_2CH_2CO_2H$ and 1.1% of $CH_3CH_2CPh(CH_3)CO_2H$, and three major unidentified volatile acids. Repetition of this reaction in ethyl ether gave 0.9% of $PhC(CH_3)_2CH_2CO_2H$ but only 0.02% of $CH_3CH_2CPh(CH_3)CO_2H$ and four unidentified volatile acids.

(c) Reaction with 1-Chloro-5-phenylpentane. — This halide with some 50 to 200% excess Cs-K-Na alloy at -65° for 19 minutes in tetrahydrofuran gave, upon carbonation, 12 to 15% yield of 6-phenylhexanoic acid, 3 to 8% of phenylacetic acid, and 4 to 26% of an acid which is tentatively identified as 3-phenylpropanoic acid (since ethylbenzene is found in the products of alcoholysis of the organoalkali reagent). Contact of this halide with the alloy gives an almost immediate intense red color. This observation and the increased yield of the acid corresponding to 5-phenylamyl anion over the yield of normal product with n-butyl chloride and neophyl chloride suggest that some stabilization by phenyl is being observed such as in I or a weaker stabilization as in II.



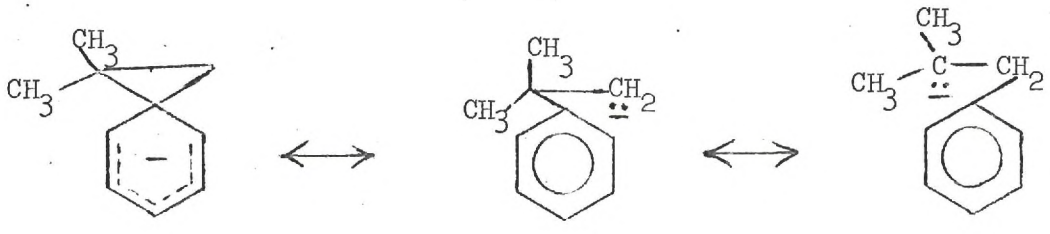
I II

The presence of phenyl acetic acid and 2-phenylpropanoic acid in the products demonstrates the interesting fact that fragmentation[4] of C-C bonds occurs readily even at -65°. The appearance of benzyl anion in the products is not surprising since this anion is well stabilized by resonance; the probable appearance of 2-phenylethyl anion is more surprising and suggests that this anion is stabilized possibly as III or IV. The low yield of



III IV

neophylcesium, observed earlier, can be rationalized in terms of competing reactions involving the β,β'-dimethyl groups or, alternatively, in terms of destabilization of the anion by these groups possibly because of destabilization of structure VC.

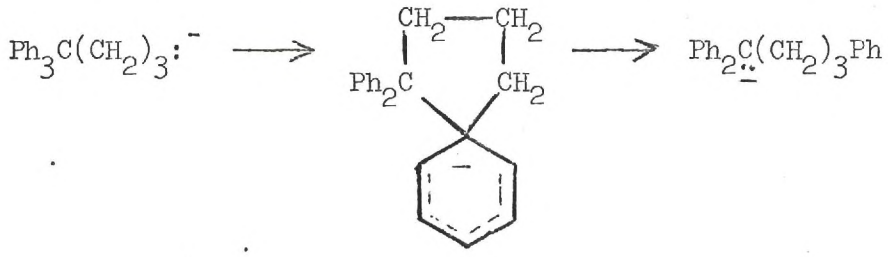


VA VB VC

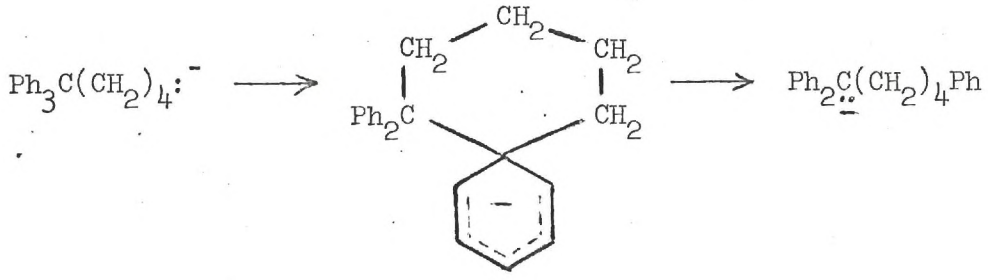
(4) R. A. Finnegan [Trans. N. Y. Acad. Sci., 27, 730 (1965)] has observed fragmentations of organopotassium compounds suspended in hydrocarbon media at room temperature, although this type of reaction is not well documented.

(d) Reaction with 4-Chloro-1,1,1-triphenylbutane and 5-Chloro-1,1,1-triphenylpentane.[5] — Reaction of 100% excess of Cs-K at -42° with 4-chloro-1,1,1-triphenylbutane in tetrahydrofuran for about 45 minutes followed by rapid addition of a large excess of methanol gave 32% yield of 1,1,1-triphenylbutane, 30% of 9-phenyl-9-n-propylfluorene, 20% of 9-phenyl-9-n-propyl-2,4a,4b,7-tetrahydrofluorene, and 8% of 1,1,4-triphenylbutane. Similar reaction of 5-chloro-1,1,1-triphenylpentane with Cs-K-Na alloy at -65° in tetrahydrofuran gave 8% of 1,1,1-triphenylpentane, 20% of 9-butyl-9-phenylfluorene, 67% of 9-butyl-9-phenyl 2,4a,4b,7-tetrahydrofluorene, and 5% of 1,1,5-triphenylpentane.

The most interesting result from this work is that 1,4- and 1,5-migration of phenyl have been observed presumably by way of intermediates VI and VII:



VI

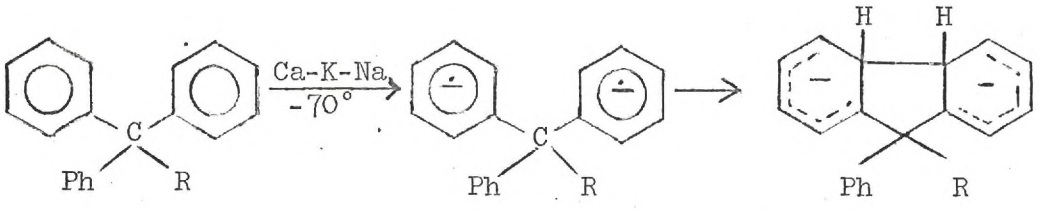


VII

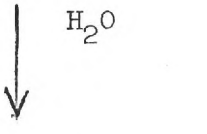
(5) This work (Grovenstein, Pegolotti, and Cheng) was presented at Metrochem 69 Regional Meeting, Amer. Chem. Soc., May, 1969, p. 39 of abstracts.

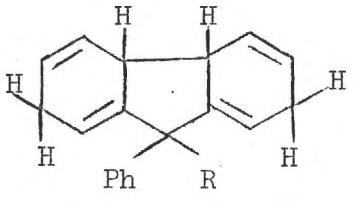
The yields of these rearrangement products are, however, only some 5 to 10%. The major products appear to arise by protonation of the unrearranged carbanions (protons being supplied by tetrahydrofuran) to give 1, 1, 1-triphenylbutane and 1, 1, 1-triphenylpentane which are then further reduced by the alkali metals to give fluorene derivatives (see later discussion). The low yield of products of rearrangement can be explained on the basis that cyclization to VI and VII is made difficult by steric effects (thus in VII two bulky groups are necessarily axial) such that the carbanions are largely destroyed by interaction with solvent prior to rearrangement.

(e) Reaction with 1, 1, 1-Triphenylethane and 1, 1, 1-Triphenylpentane. - The reaction of 1, 1, 1-triphenylethane with a 16-fold ratio of Cs-K-Na alloy to hydrocarbon in tetrahydrofuran at -70° gave a deep red solution which upon jetting into ice-water gave a single major product characterized as 9-methyl-9-phenyl-2, 4a, 4b, 7-tetrahydrofluorene. 1, 1, 1-Triphenylpentane gave a similar reaction. These reactions can be explained by the sequence:



VIII IX





9-Alkyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene

The red intermediate is believed to be IX. Upon titration with methanol, this red anion consumed exactly two equivalents of methanol before disappearance of the red color. If the red intermediate can be fully established as IX (rather than, say, VIII), the present example would appear to be the first instance of "isolation" of such a structure although 6,6-dialkylcyclohexadienyl anions are known. This also appears to be the first example of a reductive cyclization of unconjugated aromatic rings.

(f) Reaction with 4-Chloro-1-(p-biphenylyl)-1,1-diphenylbutane. - This compound is presently being synthesized in order that its reaction with Cs-K-Na alloy may be studied. It is known[6] that p-biphenylyl undergoes 1,2-migration much more readily than m-biphenylyl in 2-m-biphenylyl-2,2-bis(p-biphenylyl)-ethyllithium. Hence we wish to see if the migratory aptitude of p-biphenylyl is great enough in 1,4-migration so that migration will become the major reaction (contrast the case of phenyl migration in 4,4,4-triphenylbutyl anion in previous discussion).

II. Preparation and Rearrangements of Organolithium Compounds in Tetrahydrofuran

(a) Neophyllithium. - Reaction of neophyl chloride with lithium in tetrahydrofuran at -65° gives about 80% yield of organolithium agent which consisted of about 95% 2-methyl-2-phenylpropyllithium and 5% 1,1-dimethyl-2-phenylethyllithium. Upon long standing or warming up to 4°, the tertiary lithium compound is readily converted to isobutylbenzene and the primary compound less readily to t-butylbenzene, but no additional product of 1,2-phenyl migration is observed. These and other more detailed results are interpreted to mean that neophyl chloride reacts with lithium metal to give first neophyl

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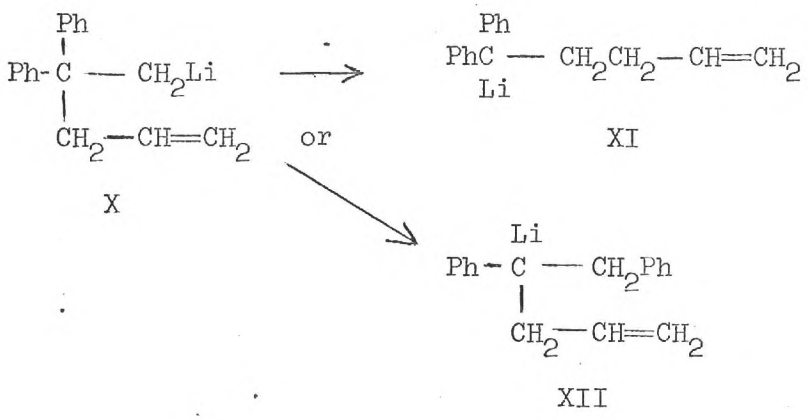
(6) E. Grovenstein, Jr., and G. Wentworth, J. Am. Chem. Soc., 89, 2348 (1967).

radical which is in part free enough from the metal surface to rearrange (1,2-phenyl migration) to 1,1-dimethyl-2-phenylethyl radical. Further reduction of the radicals by lithium metal results in the observed organolithium compounds. This work has contributed substantially to our knowledge of the mechanism of reaction of primary alkyl chlorides with lithium metal.[7]

(b) 2,2-Diphenyl-4-pentyllithium. — This organolithium reagent has been prepared by reaction of the corresponding chloride with lithium metal in tetrahydrofuran. Upon warming to 0° the lithium compound undergoes rearrangement to give a red compound whose structure is under investigation. It is anticipated that the lithium reagent X can undergo either 1,2-migration of



allyl to give XI or, less likely, 1,2-migration of phenyl to give XII. If allyl migration occurs, we will label one end of the allyl system with C-14 in order to see if rearrangement occurs with retention of position of label, allylic inversion of position of label, or scrambling of label at both ends of allylic system.

(c) 2-(p-Biphenylyl)ethyllithium. — Synthesis of this reagent has so far proceeded only to the stage of 1-chloro-2-(p-biphenylyl)ethane, which is prepared from 4-acetylbiphenyl. We deem study of this reagent of interest to see

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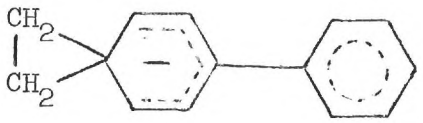
(7) Our work upon neophyllithium has recently been submitted for publication in Chemical Communications.

if rearrangement is possible in a lithium reagent in which the product of rearrangement is no more stable than (in fact, identical to) the starting reagent. Ultimately the starting 1-chloro-2-(p-biphenylyl)ethane will be labeled at the 1-position with deuterium in order that rearrangement, if any, may be detected. In previous cases of rearrangement of organolithium compounds, the product of rearrangement has always been more stable than the starting organolithium reagent because of relief of steric strain or electron delocalization. Also in all previous cases of 1,2-shift of aryl there were three beta-substituents so it is not clear that side reactions (e.g., loss of LiH) will not complicate the present example. The choice of 1-biphenyl was made in order to have a stable hydrocarbon group of as high a migratory aptitude as possible. It is hoped that the suspected intermediate XIII will be sufficiently stable so that it may be

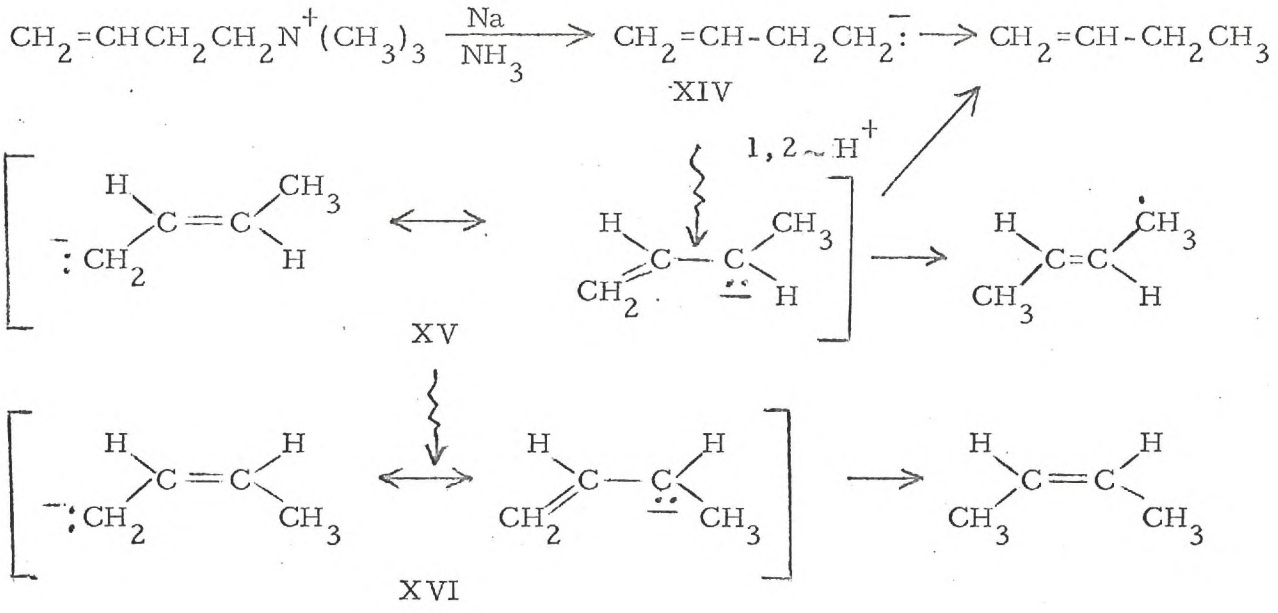


XIII

detectable by spectroscopic means; if this is not true for the lithium compound it may be true for the cesium compound which will also be studied.

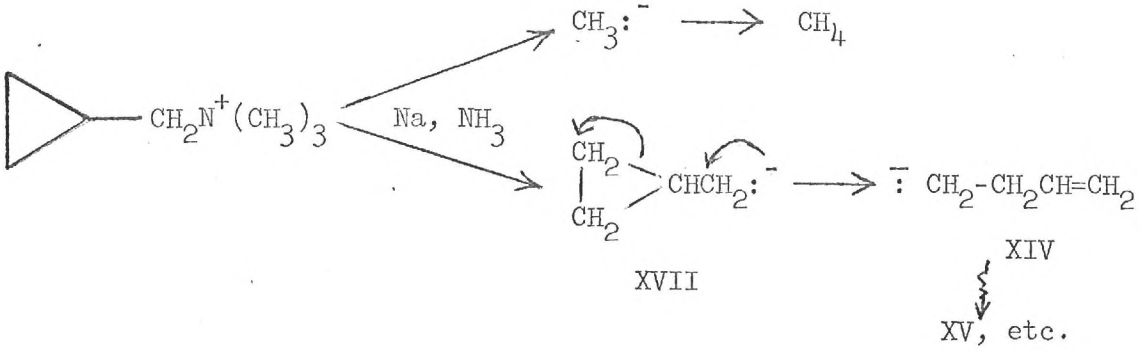
III. Preparation and Rearrangement of Unstable Organosodium Compounds in Liquid Ammonia

Cleavage of homoallyltrimethylammonium bromide by sodium in liquid ammonia gave a mixture of hydrocarbons consisting of CH_4 (0.2%), butene-1 (0.9%), trans-2-butene (82%), cis-2-butene (16%), and butadiene (1.3%). This mixture of products is tentatively accounted for by the scheme:



Some support for this scheme comes from the observation that addition of methanol increases the yield of butene-1 to 25.5% of the hydrocarbons produced, reduces the yield of cis-2-butene to 0.6%, and reduces the yield of butadiene to 1.0%. Methanol is expected to trap intermediate carbanions by protonation. The increase in yield of butene-1 is ascribable to trapping of the homoallyl anion XIV; the decrease in yield of cis-2-butene to trapping of its precursor trans-crotyl anion XV. The most interesting step of the proposed machanism involves the, apparently previously unknown, rearrangement of homoallyl anion XIV to trans-crotyl anion XV; it is not known whether this is an intra- or intermolecular process. Further it should be stressed that the detailed structure of the homoallyl anion is unknown; we have written the classical structure only for the sake of simplicity.

Cleavage of cyclopropylcarbinyltrimethylammonium ion by sodium in liquid ammonia produces predominately methane and a mixture of hydrocarbons about like that from the homoallylammonium salt. This observation suggests that the cyclopropylcarbinyl anion XVII rearranges readily to the homoallyl anion XIV which then rearranges further as described above.



Again, it must be stressed that it is not known whether the intermediates called here cyclopropylcarbinyl and homoallyl anions are separate distinct species as implied or whether a single substance of a non-classical structure is involved.

The cyclopropylcarbinyl to homoallyl rearrangement has been previously studied by Roberts and co-workers for the case of the corresponding Grignard reagents and by Lansbury and co-workers for the corresponding lithium reagents. Since Grignard and lithium reagents normally have considerable covalent character for the carbon-metal bonds, it is not clear whether generalizations based on these organometallics can be applied to the more ionic sodium compounds in liquid ammonia solution.

Additional work needs to be done on the detailed mechanism of the present cleavages in liquid ammonia and upon the structure of the intermediates. It is planned for the new work to include a study of cleavage of cis- and trans-crotyl and cyclobutyl quaternary ammonium salts. Also isotopic tracer studies will be performed to ascertain whether the rearrangements are intra- or intermolecular (especially for hydrogen migration) and to tell how extensively the carbon atoms become scrambled.

Personnel:

In addition to the Principal Investigator the work described in this report has been conducted by the following: Mr. Yao-Ming Cheng (graduate research assistant, supported by the present grant throughout the entire grant period), Mr. Jung-Ung Rhee (graduate research assistant, supported for the past three months by the present grant), and Dr. Craig L. Smith (post-doctoral research assistant, supported for the three months by the present grant and six months by funds from the Georgia Institute of Technology). In addition to the above, the work described in this report was substantially contributed to by Mr. Auburn B. Cottingham (NSF Trainee) and by the following NSF Summer Research Participants: Dr. James A. Pegolotti, Dr. John A. Kaczynski, and Dr. James A. Beres.

Finally, with permission from the National Science Foundation, funds from the present grant were used for six months to support Mr. Tomoo Shibata as a graduate research assistant. Since Mr. Shibata's work was in another area of chemistry and has already been published[8] in large part, it will not be described here.

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(8) "Photochemical Reactions of Dimethyl Acetylene-dicarboxylate with Benzene and Naphthalene," E. Grovenstein, Jr., T. C. Campbell, and T. Shibata, J. Org. Chem., 34, 2418 (1969)

TO: Dr. Donald A. Speer, Director
Chemical Dynamics Program
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr., Principal Investigator
School of Chemistry, Georgia Institute of Technology

SUBJECT: Final Technical Report upon "Chemistry of Carbanions"
NSF Grant No. GP-8309
For Period April, 1968-April 30, 1970

Brief Description of Research and Results[1]

A new preparation of organoalkali compounds by use of the alloys of cesium and potassium has been developed. Alkylcesium (potassium) compounds are unstable in ethereal solvents even at -65°; proton abstraction from the solvent and various fragmentation reactions have been observed.

In the reaction of 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylpentane with Cs-K or Cs-K-Na alloys in tetrahydrofuran, 1,4- and 1,5-migration of phenyl respectively have been observed. The major product of these reactions, however, is formed by proton abstraction from the solvent to give 1,1,1-triphenylbutane and 1,1,1-triphenylpentane respectively, followed by reductive cyclization to give a red dianion which upon decomposition with water yields 9-alkyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene.

The synthesis of 4-chloro-1-p-biphenyl-1,1-diphenylbutane has now been accomplished. Studies upon the reaction of this chloride with Li, K, and Cs-K-Na alloy will soon begin in order to see if the migratory aptitude of p-biphenylyl is great enough so that 1,4-migration of p-biphenylyl will now become the major reaction of the initial carbanion.

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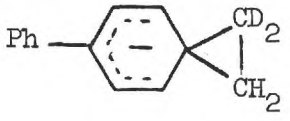
(1) For further details upon this work see our "Resumé of Progress to Date upon 'Chemistry of Carbanions'" for period of April 1, 1968 to Sept. 30, 1969. This was prepared for our grant renewal application; a copy of this is enclosed.

A partial rearrangement of phenyl during the reaction of neophyl chloride with lithium in tetrahydrofuran at -65° has been observed. This result is interpreted to mean that neophyl chloride reacts with lithium metal to give first neophyl radical which is in part free enough from the metal surface to rearrange to 1,1,dimethyl-2-phenylethyl radical before further reduction with lithium metal to give the observed organolithium compounds.[2]

1-Chloro-2-biphenylylethane-1,1-$\underline{d}_2$ has been synthesized and reacted with various alkali metals in tetrahydrofuran. With lithium metal only unrearranged 1-lithio-2-$\underline{p}$-biphenylylethane-1,1-$\underline{d}_2$ or unrearranged products derived therefrom were obtained from -65 to 2°. With molten potassium, however, in refluxing tetrahydrofuran about a 1:1 mixture of 1-$\underline{p}$-biphenylylethane-2,2-$\underline{d}_2$ and 1-$\underline{p}$-biphenylylethane-1,1-$\underline{d}_2$ was produced. This result seems to imply the formation of the intermediate bridged carbanion or radical, shown below as the carbanion:



A preliminary study of the reaction of the present chloride with Cs-K-Na alloy at -70° in THF indicated no rearrangement in the 1-$\underline{p}$-biphenylylethane produced. The occurrence or non-occurrence of rearrangement in this system appears to be a sensitive function of metal, temperature, and probably solvent.

Publications

(1) "Photochemical Reactions of Dimethyl Acetylenedicarboxylate with Benzene and Naphthalene," E. Grovenstein, Jr., T. C. Campbell, and T. Shibata, J. Org. Chem., 34, 2418 (1969). The permission of the National Science Foundation to support Mr. Tomoo Shibata under the present grant for six months in this unrelated area of chemistry was greatly appreciated and permitted completion of this work.

(2) "Phenyl Migration during Reaction of Neophyl Chloride with Lithium," E. Grovenstein, Jr., and Y.-M. Cheng, Chemical Communications, 101 (1970).

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(2) E. Grovenstein, Jr., and Y.-M. Cheng, Chemical Communications, 101 (1970).

Additional publications are planned to cover the other research described in this progress report; in most cases, however, additional experiments need to be performed to complete the work.

Theses

(1) The Ph.D. theses of Y.-M. Cheng should be completed by the end of the summer, 1970.

(2) The M.S. thesis of T. Shibata (on photochemistry) should be completed by the end of the summer, 1970.

(3) The Ph.D. thesis of J. V. Rhee is still in its early phases.

Inventions or Discoveries

Most of the research effort has been devoted to extending our knowledge of carbanion (and free radical) rearrangements. While this research is of both theoretical and practical importance, it is not in general of the type for which patents are sought. Some of the research with cesium alloys which was begun under the present grant and is continuing under the grant renewal may prove to be worth patenting.

Scientific Collaborators

Mr. Yao-Ming Cheng - Ph.D. candidate, 25 months of support on the grant.

Mr. Jung-Ung Rhee - Ph.D. candidate, 10 months of support on the grant.

Dr. Craig L. Smith - Post-doctoral research assistant, 3 months of support on the grant.

Mr. Tomoo Shibata - M.S. candidate, 6 months of support on the grant.

Dr. James A. Pegolotti, Dr. John A. Kaczynski, and Dr. James A. Beres - These were NSF Summer Research Participants who worked in the area of the grant (but were <u>not</u> directly supported by the grant) under the supervision of the Principal Investigator who <u>was</u>, for two summer months, directly supported by the grant.

Comments

This investigation is being continued under NSF Grant No. GP-19251.

Erling Grovenstein, Jr.
Principal Investigator
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